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SOLUTIONS

DONALD KITELEY TRESSLER

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BY
DONALD KITELEY TRESSLER

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THE SOLUBILITY OF THE SOIL POTASH IN VARIOUS SALT SOLUTIONS¹

DONALD KITELEY TRESSLER

Bureau of Fisheries, United States Department of Commerce

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HISTORICAL

In this the day of extremely high-priced potash when the supply of potash does not keep up with the demand, the question of whether other elements can unlock potash from the insoluble minerals of the soil is of vital importance. If there are minerals which can liberate soluble potash from some of the insoluble minerals of the soil and thus make available for the use of the plant the immense stores of mineral potash which the soil contains, they should be commended for the use of the farmers.

The various text-books contain many conflicting statements in regard to the power of sodium, calcium and magnesium to replace potassium. It is the purpose of this work to clear up this point, if possible.

The up-to-date publications on soil fertility were examined and it was found that the following said that lime replaced some potash in the soil: Aikman, Blair, Halligan, Hall, Hart and Tottingham, Ingle, Lincoln and Walton, Van Slyke, Vivian, and Voorhees. Briggs and Breazeale, Gaither and Keitt and King and Curry and Smith were dubious as to whether any replacement took place.

The authors who were of the opinion that gypsum replaced potash are listed as follows: Snyder, Hilgard, Aikman, Hopkins, Keitt and King, Ingle, Voorhees and Van Slyke. Harter, Curry and Smith and Murray do not seem to have much faith in the power of calcium sulfate to set free potash.

There is more disagreement among the writers in regard to the action of common salt than as to the action of the calcium compounds. Aikman, Curry and Smith, Snyder, Hall, Storer, Lyon, Fippin and Buckman, and Van Slyke credit common salt with the power of replacing potash in soils. Hart and Tottingham, Voorhees, Murray, and Roberts are doubtful as to the power of salt in this regard.

The question of the liberation of potash is not a new one. E. Wolff [cited by Storer (21)] about 1850 was probably the first to point out the possibility that potash might be replaced by the soda of common salt. He grew a field of buckwheat, one half of which he manured heavily with common salt while

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the other half was unmanured. On analyzing the ashes of the buckwheat straw he found that the portion of the crop that had received the salt contained less soda but more potash than the other. (The statement that Wolff was the first to point out the possibility of the replacement of potash by soda in soil, does not infer that Wolff was the first to use common salt as a manure. At that time salt was quite a common manure in England and France, but its value was somewhat debated. In doing his work Wolff was working on the theory of mineral nutrition of plants.)

Boussingault in about 1860 showed the effect of lime and gypsum on the clover grown on some soils, by analyzing the ash of limed and unlimed clover and also plastered and unplastered clover. His results are given in the following tables [cited by Halligan (13)]:

Composition of clover ash

| | KILOS PER HECTARE | | | |
|----------------------|-------------------|-------------|------------|-------------|
| | Unlimed | | Limed | |
| | First year | Second year | First year | Second year |
| Lime..... | 32.2 | 32.2 | 79.4 | 102.8 |
| Potash..... | 26.7 | 28.6 | 95.6 | 97.2 |
| Phosphoric acid..... | 11.0 | 7.0 | 24.2 | 22.9 |

Composition of clover ash-gypsum tests

| | WITHOUT GYPSUM | WITH GYPSUM |
|-----------------------------------|-----------------|-----------------|
| | <i>per cent</i> | <i>per cent</i> |
| Potash..... | 23.6 | 35.4 |
| Soda..... | 1.2 | 0.9 |
| Magnesia..... | 7.6 | 6.7 |
| Lime..... | 28.5 | 29.4 |
| Oxides of iron and manganese..... | 1.2 | 1.0 |
| Chlorine..... | 4.1 | 3.8 |
| Phosphoric acid..... | 9.7 | 9.0 |
| Sulfuric acid..... | 3.9 | 3.4 |
| Silica..... | 20.0 | 10.4 |

In the first table it is seen that the percentage of potash in the ash increases more than the percentage of lime. It hardly need be pointed out that the increase of the percentage of potash in the ash might be due to other factors than the liberation or replacement of potash by the lime or the gypsum.

Considerable work was accomplished on the solubility of the soil potash in various salt solutions about the year 1860. Dietrich (7) performed some experiments concerning the solubility of soil constituents in various solutions. He found that the alkali metals of the soil were much more soluble in water containing carbon dioxide than in pure water. He found that calcium car-

bonate dissolved in carbonic acid solutions dissolved about the same amount of total alkalis as did carbonic acid of equal strength. In later work (8) Dietrich found that N/20 solutions of sodium chloride, calcium chloride and lime dissolved much more potassium from soils than did pure water. He found that sodium nitrate and sodium carbonate solutions did not dissolve potash. He concludes that by the manuring of a field with common salt, important amounts of potash are set free.

Eichhorn (9) in 1858 tried the solvent powers of sodium chloride solutions and found that somewhat more potash was dissolved in these solutions than in water. Beyer (2) tried the action of various solutions on feldspars and measured the amount of potash dissolved. Calcium sulfate was not found to have any marked effect on the potash. Sodium chloride solutions and also the nitrate solutions were found to exert a powerful solvent effect on the potash. Sodium nitrate was less active than the chloride.

Harry Snyder (19) in 1893 came to the following conclusion as a result of his experiments on the soils of Minnesota.

The indirect action of land plaster (gypsum) on these soils (western and central prairie soils—black soils resting on yellow clay) in liberating plant-food, particularly potash and phosphoric acid, is unusually marked. Experiments conducted in this laboratory have shown that small amounts of gypsum are quite active in rendering potash, phosphoric acid and even nitrogen soluble in the soil water. It is not the land plaster itself that furnishes the food, but it is the power that it possesses in making mineral matters available that are already in the soil. Land plaster acts more as a stimulant and not as a direct fertilizer, and if not used to excess it will be a profitable fertilizer to use on these soils, especially to bring in grass and clover.

The writer has been unable to find any further reference to the laboratory work which Snyder says was performed at the Minnesota Agricultural Experiment Station.

The Rothamsted Experiment Station has been carrying on experiments concerning the manuring of mangels with soda since 1876. The results (12) seem to indicate that manuring with common salt increases somewhat the percentage of potash in the mangels, but it also increases greatly the percentage of soda in the mangels. The yield of the crop was greatly increased by the addition of soda. The total amount of potash in the crop of mangels was in most cases increased by about one-half. Hall, in discussing these experiments, states that this increase is due to the attack of the soda salt upon the insoluble potash of the soil. The conclusion which Hall (11) draws is quoted as follows:

Since soluble alkaline salts are beneficial to the mangel crop either as direct foods or as economizers of potash, a dressing of salt should always be included among the manures for the mangel crop.

Wheeler (23) in drawing conclusions from the experiments (24, 25, 26, 27, 28, 29) with sodium salts at the Rhode Island Experiment Station, says:

As a result it appeared that possibly unable to wholly replace potassium in any one function, or at least in all of its functions, in connection with the growth of certain plants, sodium may and often does perform some part of one or more of the important functions of potassium and thus increase the amount of dry matter which the plant can produce.

The experiments referred to have been over a period of more than twenty years. Wheeler thinks that the most important function of the sodium salts is not, therefore, the action on the potash-bearing minerals of the soil, but rather as a direct plant nutrient.

Curry, Smith and others (6) of the New Hampshire Agricultural Experiment Station have carried out a large number of experiments relative to the solubility of potash in various salt solutions. They percolated solutions of lime, sodium chloride, sodium carbonate, sodium nitrate, acid phosphate and other salts through columns of soil. They stirred feldspar with these various solutions and also stirred a mixture of feldspar and clay with the solutions. They tried the solubility of feldspar in solutions of lime, gypsum, sodium nitrate, ammonium sulfate, sodium carbonate and disodium phosphate. They found that all of these salts increased the solubility of the potash contained in the feldspar, lime having the greatest solvent action. However, when the feldspar was mixed with clay the lime solution had even less solvent action than pure water. They observed that when solutions of sodium nitrate, sodium chloride, sodium carbonate and acid phosphate are percolated through columns of soil more potash is made soluble than when water is percolated. They conclude that calcium carbonate and lime have practically no effect on the solubility of the soil potassium, and that the calcium sulfate makes but small amounts of potassium soluble. However, they say that the effect of sodium chloride, sodium nitrate, sodium carbonate and acid phosphate is to greatly increase the solubility of the soil potassium. The reaction, they believe, between these salts and the soil is chemical.

Soderbaum (20), working on plot experiments in 1911, however, concluded that the beneficial results obtained from the use of common salt as a fertilizer were due to the effect of the chlorine which was introduced and not to the sodium.

Bradley (3) of the Oregon State Agricultural College worked on the effect of lime and gypsum upon the soils of Oregon. He mixed the soils with either lime or gypsum in large glass percolators and allowed the soils to stand at the optimum moisture content for six weeks. He analyzed the solutions obtained by leaching these soils. He found that both lime and gypsum set potash free. The gypsum, however, was more active in this regard than the lime. He also tried shaking the soils with solutions of lime and gypsum. In this case he found that the lime decreased the amount of potash going into solution, whereas the gypsum increased it greatly. He concludes that gypsum sets free potash in the soils of the Willamette Valley.

Gaither, of the Ohio Agricultural Experiment Station (10) working with plot tests determined the solubility of the various elements in N/5 nitric acid.

He concludes that lime breaks up certain silicates in the soil and renders them more soluble in N/5 nitric acid but does not act upon the insoluble potassium compounds in the soil to such an extent that N/5 nitric acid can be used as a measure of such potash. The addition of caustic lime has the effect of diminishing the amount of potash assimilated by wheat grown on such soil. The theory that lime added to the soil increases the amount of available potash in the soil is either erroneous or requires more positive proof than has heretofore been obtained, before it can be accepted.

Andre (1) in 1912 worked on the replacement of potash in certain feldspathic rocks by the addition of sea salt or of sodium nitrate. He found that the potash of microcline was quite noticeably dissolved by solutions of sea salt or sodium nitrate; the amount of potash going into solution being almost the same in both cases. He concludes that the replacement explains the favorable action of salt when used as a fertilizer. He thinks that sodium nitrate is valuable as a fertilizer not only for the nitrogen that it furnishes, but also because the sodium added to the soil sets free a certain amount of potash.

Iakushkin (16) found that the addition of sodium chloride as a fertilizer increased the yield of Japanese millet 52 per cent. The beneficial effect of sodium was observed in a complete normal nutrient solution, thus indicating that the action of sodium is not due to the replacement of potash.

Hartwell and Wessels have published data (14) concerning the experiments at the Rhode Island Agricultural Experiment Station of a more recent date than that of Wheeler previously referred to. They observe that soda can partially replace potassium as a fertilizer for mangels and onions. If liberal applications of sodium manures were applied, an equally large yield of onions and mangels were obtained even when the amount of potash manures had been reduced one-third. However, when the potash ration was reduced one-half, in some cases the crop yield was reduced somewhat.

Briggs and Breazeale (4) of the Bureau of Plant Industry, have recently finished some work which seems to prove the opposite of much of the work which has been cited. Their article in the *Journal of Agricultural Research* excited considerable comment and a number of persons, including the writer, have attempted to duplicate the results which they reported. They determined the solubility of pegmatite and orthoclase in calcium hydroxide and calcium sulfate solutions of various concentrations. The calcium hydrate solutions did not modify the solubility of the potassium in either pegmatite or orthoclase. Gypsum solutions depressed the solubility of the potassium in orthoclase, the quantity of potash in the solution decreasing progressively as the concentration of the calcium sulfate solution increased.

Similar tests were made upon a virgin soil of a granitic type. The solubility of the potash was not measurably different in distilled water and in solutions of calcium sulfate or calcium hydroxide. In the case of a soil of similar nature, which had been under cultivation for some time, which was somewhat more

granular and less weathered than the virgin soil, the addition of calcium sulfate decreased the solubility of the potash. They conclude:

The experiments indicate that the availability to plants of the potash in soils derived from orthoclase-bearing rocks is not increased by the addition of lime or gypsum. In some instances a marked depression of the solubility of the potash in the presence of gypsum was noted.

In some recently published work (17) concerning some lysimeter experiments, Lyon and Bizzell have shown that the application of lime to soils did not result in an increase in the quantity of potash contained in the drainage water, nor in any increase in the amount of the potassium contained in the crops.

From the foregoing review of the literature, it is seen that about the year 1860 it was generally accepted that calcium and sodium salts did liberate potash from the soil. Although this was accepted as a fact, insufficient proof was given. Recently Wheeler has suggested that perhaps the plant did not derive its benefit from the potash set free when salt was applied to the soil, but from the element itself. Within the last decade a number of experimenters have again attacked the problem of liberation of potash. Different men have obtained different results. There is not the agreement of results from which the truth can be deduced. The writer wishes to point out that the various workers have used different types of soil and that it is but natural that they should get different results. No general statements can be made from the experimental work performed with one type of soil. Experimenters should use many types of soil from many localities and then draw their conclusions for the types of soil used in their experiments.

EXPERIMENTAL

In this work no effort was made to determine the nature of the phenomenon of the liberation of potash from the soil minerals by the salt solutions. The writer determined the amount of potash that dissolved in salt solutions. An attempt was made to determine the effect of the concentration of the solution. Various types of soils were studied with particular reference to the effect of solutions of calcium sulfate upon the potash which they contain. Besides studying the effect of the various calcium salts upon the soil potash, the effects of various sodium salts were studied.

The solubility of the soil potash in carbonic acid and in calcium bicarbonate was compared, in order to throw some light upon the action of lime or calcium carbonate upon the potash contained in the soil minerals.

Soils which had been manured with gypsum for years were compared in regard to the solubility of the soil potash in gypsum solutions with check soils, which had never been treated with gypsum. It was hoped that this might give some information on the residual effect of gypsum as a fertilizer.

THE METHOD

The method used in the experiments was practically the same in all cases. It consisted in merely allowing the soil to remain in contact with the various salt solutions until the systems came to equilibrium. One hundred and twenty five grams of dry soil, or its equivalent in moist soil, was placed in a liter of water contained in a 2-liter bottle. Various amounts of salts were added to the solutions and they were allowed to stand for 3 weeks. During this period they were shaken once or twice a day. In order to determine whether the soil potash was more or less soluble in the salt solutions, blank determinations were run in all cases. In other words, no salts were added to some of the soil samples but the soil was merely allowed to stand in contact with the water under the identical conditions.

In case this procedure was altered in any way, it is noted in connection with the results.

It was determined by experiment that at least 2 weeks are required for the soil to come into equilibrium with the solution. At the end of a week the amount of potash found in one of the solutions was 2.1 parts per million. At the end of 2 weeks the same solution contained 3.2 parts of potash per million and at the end of 3 weeks the amount had not changed perceptibly. In order to be reasonably sure that the soil was in equilibrium or nearly so with the solution, the solutions were allowed to remain in contact with the soil for 3 weeks. At the end of that time the solutions were decanted off from the soil and were filtered through a Pasteur-Chamberland porcelain filter.

Potash was determined in the solutions. The method used was a modified Cameron and Failyer method. This method was first described by the above men in the *Journal of the American Chemical Society* (5). To an aliquot of the solution some ammonium oxalate solution and a couple drops of a 10 per cent ammonium carbonate solution were added. The amount of ammonium oxalate added depended upon the amount of calcium in the solution. If no calcium salt was added only three or four drops of a saturated solution of ammonium oxalate was added. The solution was then heated to boiling and boiled for a minute and then filtered. The filtrate was collected in an evaporating dish and the solution evaporated to dryness on a water bath. Enough dilute sulfuric acid was then added to moisten the salts and the dish was then heated at a dull red heat until the ammonia was completely driven off.

The salts were then taken up in a little water, a drop of pure concentrated hydrochloric acid was added, and then sufficient 0.25 per cent chloroplatinic acid to react with all the sodium and potassium salts present, after which the solution was evaporated to a paste on a water bath. The paste was then taken up in alcohol. Ninety-five per cent alcohol was used, for the potassium chloroplatinate is less soluble in alcohol of that strength than it is in 80 per cent alcohol. The solution was then filtered through asbestos into a Gooch

crucible. The potassium chloroplatinate was well washed with alcohol. When no large amount of sodium was present 100 cc. of alcohol were used. But when sodium salts were added to the solution it was found necessary to wash the chloroplatinate with 150 cc. of alcohol in order to dissolve all of the sodium chloroplatinate. After drying the crucible in an oven at 100° for a half-hour, the potassium chloroplatinate was dissolved in about 50 cc. of hot water and a drop of concentrated hydrochloric acid was added. After cooling, a solution of potassium iodide containing at least ten times more than enough potassium iodide to react with the chloroplatinate was added and the solution allowed to stand over night. During this time a rose color developed in the solution and the next morning the color was compared in a colorimeter with a standard solution containing a known amount of potassium chloroplatinate prepared in a similar manner. The most trouble was experienced in obtaining checks when sodium salts were present in large quantity.

When no sodium had been added to the solution no trouble was found in getting the determinations to check within 0.5 part per million. When large amounts of sodium were present checks were usually within one part per million.

DESCRIPTION OF SOILS

The soil called Dunkirk silt loam which was used in many of the experiments is a light brown silt loam. It belongs to the "Glacial lake and river terrace province." It is underlain by a slightly heavier subsoil of a brown color. It is of a sedimentary origin and represents the wash from the higher slopes deposited in quiet glacial lake waters. It is a good soil for general crops. That used in the experiments contained 4.7 per cent of organic matter (determined as loss on ignition) and 1.9 per cent of potash. It was slightly acid to litmus paper. It was obtained near Ithaca, New York.

The soil called Whiteland clay subsoil was obtained in the town of Corvallis, Oregon. It belongs to the second bench Willamette type. It is of sedimentary origin and was laid down by the Willamette River. Whiteland is a poorly drained soil of mottled gray and brown color. It is underlain by a heavy gray clay and this is the soil used in the experiments. It contained 6.2 per cent of organic matter (determined as loss on ignition) and 1.94 per cent of potash. It reacted neutral to litmus. This is a very poor soil for all crops.

The Yamhill silt loam was obtained from near Corvallis, Oregon, and is an alluvial soil laid down by the Willamette River. It belongs to the first bench soils of the Willamette series. It is a brown loam soil with a brown subsoil of finer texture than the surface soil. It reacted neutral to litmus. The sample analyzed contained 1.5 per cent of potash and lost 4.8 per cent on ignition. It is a very fertile soil.

The Porters sandy loam belongs to the "Appalachian soil province" and is of residual origin. The sample used in these experiments was obtained from North Carolina. It is of igneous rock origin, occupies mountainous land,

and is dark gray in color. The sample used contained many small glistening scales of mica. It contained 10.2 per cent of organic matter; its potash content was 1.2 per cent, and its reaction towards litmus was neutral. The sample was from a fertile field. Wheat, corn, oats, rye and potatoes are the principal crops grown on it.

The Durham sandy loam is a soil belonging to the Piedmont soil province. The sample used in the experiments was obtained from North Carolina. The soil is a light sandy loam underlain by a pale yellow sand. The type is derived from a light-colored granite. Owing to a lack of organic matters the soil dries out quickly. The sample taken, however, contained more than the average amount of organic matter for this type—8.7 per cent. Its potash content was 0.4 per cent. It reacted slightly acid to litmus. The soil is not especially fertile.

The Genessee humus loam is a recently formed alluvial soil, formed from reworked glacial till. The sample used was obtained near Ithaca, New York. It was mottled black and brown and although it contained considerable coarse sand it also contained a relatively high proportion of clay. It was of only average fertility, although it contained 15.7 per cent of organic matter. Its reaction towards litmus was neutral.

The Merrimac fine sandy loam was obtained from the experimental plots of the Massachusetts Experiment Station, Amherst, Massachusetts. The surface soil consists of a light-brown fine sandy loam. This type occurs as narrow terraces along rivers and represents glacial flood-plain deposits. The soil is a very fertile one, and brings a high price per acre, onions and tobacco doing particularly well on it. It contains 2.2 per cent of organic matter and 1.7 per cent of potash.

The chief idea in choosing the above soils was to get a variety of soils of different types and from various sections of the United States. General deductions cannot be drawn by merely experimenting with one type of soil from only one locality.

EXPERIMENTS CONCERNING THE SOLUBILITY OF THE SOIL POTASH IN ACID PHOSPHATE SOLUTIONS

Curry and Smith (6) of the New Hampshire Agricultural Experiment Station, experimented with an acid phosphate free from potash and determined the solubility of the soil potash in a very dilute solution of this phosphate. They percolated this dilute solution through a column of soil and found that there was a considerable increase in the amount of potash in the percolate. They concluded that the effect of commercial acid phosphate when applied as a fertilizer is to greatly increase the solubility of the soil potassium. They however did not attribute the action of the acid phosphate to any one compound contained in the acid phosphate.

Commercial acid phosphate consists chiefly of a mixture of monocalcium phosphate, dicalcium phosphate, tricalcium phosphate and calcium sulfate. Any liberation of potash would be due to one or all of these compounds. Dunkirk silt loam was shaken with saturated solutions of these salts and the amount of potash in the solutions noted. The results are given in table 1.

In this and all subsequent tables the amounts of potash are expressed as K_2O in parts per million of solution.

It is seen from the table that the only substance which increases the solubility of the potash to any appreciable extent is the calcium sulfate. Yet in this same paper in which Curry and Smith state that acid phosphate is so active in liberating potash from the soil, they say that "A limited number of experiments with calcium sulfate indicate that *small* amounts of potassium are made soluble."

The results of the above experiments seem to indicate that tricalcium phosphate has little or no action on the soil potash. The same is true in regard

TABLE 1
Potash liberated in Dunkirk silt loam

| SALT | CONCENTRATION OF POTASH IN SOLUTION IN PARTS PER MILLION | |
|-----------------------------|--|------|
| | A | B |
| Merely distilled water..... | 3.8 | 3.4 |
| Calcium sulfate..... | 11.8 | 11.8 |
| Tricalcium phosphate..... | 3.2 | 3.0 |
| Dicalcium phosphate..... | 3.4 | 4.0 |
| Monocalcium phosphate..... | 1.5 | 2.0 |

A and B are duplicate experiments.

to the dicalcium phosphate while the monocalcium phosphate seems to have a negative effect. It seems therefore that if acid phosphate has any beneficial effect on soil in making potash soluble, this effect is due to the calcium sulfate which it contains.

In order to learn whether the above conclusion held for other soils, two other soils were tried with the same salt solutions. In this experiment, a Whiteland clay subsoil and a Yamhill soil were tried. The results were similar except in the case of the calcium sulfate solution. They are listed in table 2.

In these other soils the calcium sulfate does not seem to have any action in making potash soluble. In one case, the dicalcium phosphate and tricalcium phosphate seem to keep the potash from going into solution. In the case of the Yamhill soil which is coarser in texture than the other soils, these phosphates have little action on the potash. In all three soils the monocalcium phosphate apparently hinders the solution of the potash. We must conclude,

therefore, that only on certain types of soil does calcium sulfate have any action. And since calcium sulfate is the active principle of commercial acid phosphate, the same holds true of acid phosphate.

TABLE 2
Potash liberated in Whiteland clay subsoil and Yamhill soil

| SALT | CONCENTRATION OF POTASH IN SOLUTION IN PARTS PER MILLION | |
|----------------------------|--|--------------|
| | Whiteland subsoil | Yamhill soil |
| Distilled water only..... | 3.2 | 3.0 |
| Calcium sulfate..... | 3.2 | 3.2 |
| Tricalcium phosphate..... | 1.8 | 3.2 |
| Monocalcium phosphate..... | 0.9 | 0.9 |

EXPERIMENTS CONCERNING THE SOLUBILITY OF THE SOIL POTASH IN SOLUTIONS OF CALCIUM SULFATE

The above-outlined experiments indicated that all soils were not uniformly affected by calcium sulfate solutions. Seven soils, from four different states, varying widely in characteristics and properties, were taken and tested as to their solubility in saturated calcium sulfate solutions. The results are listed in table 3.

TABLE 3
Results showing solubility of soil potash in solutions of calcium sulfate

| SOIL | SOLUTION | |
|-------------------------------|------------------------|--------------------------|
| | Distilled water | Calcium sulfate solution |
| Whiteland clay subsoil..... | <i>p. p. m.</i> 3.2 | <i>p. p. m.</i> 3.2 |
| Dunkirk silt loam..... | 3.5 | 11.8 |
| Yamhill silt loam..... | 3.0 | 3.2 |
| Genessee humus loam..... | 5.5 | 7.4 |
| Merrimac fine sandy loam..... | 1.0 | 1.3 |
| Durham sandy loam..... | 4.8 | 5.7 |
| Porters sandy loam..... | 3.5 | 3.7 |

Aside from the Dunkirk silt loam, Durham sandy loam and Genessee humus loam are the only soils that showed any marked effect of the action of the gypsum solution.

Because of the extraordinary action of solutions of calcium sulfate upon the Dunkirk silt loam the writer experimented further with this soil. Five hundred grams of it were taken and separated mechanically into clay, silt and sand. The sand was considered as being composed of those particles

above 0.05 mm. in diameter; the silt, those particles between 0.05 and 0.005 mm. in diameter; and the clay all particles of smaller diameter than 0.005 mm. The soil was shaken for 12 hours to deflocculate it. The clay and silt were then separated from the sands by simple subsidence and decantation. The silt was separated from the clay by whirling the soil in the water in tubes in a centrifuge. After the separation the soil separates were dried. Thirty grams of the three separates were treated with 500 cc. of an approximately saturated calcium sulfate solution for 3 weeks. Like amounts of the separates were treated with a like amount of distilled water. At the end of 3 weeks the soil solutions were filtered and the potash determined in the solutions. The results are presented in table 4.

The sand contained but 2.2 per cent of organic matter while the silt contained practically the same amount as did the entire soil, 4.6 per cent. There was not enough of the clay left over to determine the organic matter (as loss on ignition) but the clay must have been high in organic matter, as that must have contained the organic matter which was missing from the sand. Some organic matter was probably dissolved and this would be contained in the clay.

TABLE 4

Results showing the solubility in calcium sulfate of potash in Dunkirk silt loam

| SOLUTION | SEPARATE | | | |
|----------------------|-------------|------|------|------|
| | Entire soil | Sand | Silt | Clay |
| Distilled water..... | 4.7 | 3.2 | 5.9 | 17.9 |
| Calcium sulfate..... | 8.1 | 4.7 | 8.8 | 25.1 |

It is noteworthy that although some liberation of potash occurs in all three separates, the greater portion of the liberation occurs in the clay. As the particles become smaller the solubility of the potash increases and the amount made soluble by the gypsum increases.

In the above experiment the amount of potash dissolved by water alone was higher than in the previous experiments. This experiment was carried out in hot weather, whereas the previous experiments were conducted during cold weather. This was one of the factors which caused the increased solubility of the soil in distilled water.

Way (22) in 1850 found that soil absorbed potash. Solutions of potassium nitrate were filtered through columns of soil and the percolate contained no potash. In the above experiments the soil was treated in a fine suspension in solution and was well shaken so that the clay, which possesses most of the absorbing power of the soil, was entirely in suspension. It is conceivable that when a solution of calcium sulfate slowly percolates through the soil, as is the case when gypsum is added to the soil as an amendment, the gypsum may liberate the potash and have it remain in the soil. In fact, it would be sur-

prising if we would have any very large amount of potash in the drainage water from any lysimeter containing a heavy clay soil. The fact, then, that the analysis of water from lysimeter tanks does not show an increased amount of potash in solution due to the addition of gypsum to the soil does not necessarily prove that there is no liberation of potash by the gypsum. Experiments such as the above, in the writer's opinion, would be more positive proof that potash is made more soluble. For if the potash were liberated there would be little chance for the clay to absorb it and remove it from solution.

Insufficient work has been done to make it possible to state definitely in just what soils a marked replacement of potash could be expected. The Porters sandy loam was of average potash content (1.2 per cent) and even contained a large number of flakes of mica, yet there was practically no replacement of potash. Curry and Smith and others have found that gypsum solutions will dissolve some potash from the natural potash-bearing rocks, but the amount is small. The writer is of the opinion that the action on the clay is much more important. It seems probable that there will be an increase in the solubility of the potash due to calcium sulfate in fertile clays and loams containing a considerable amount of potash.

TABLE 5

Results showing liberation of potash from Dunkirk silt loam by different concentrations of calcium sulfate

| | CONCENTRATION OF SOLUTIONS | | | | |
|---|----------------------------|--------------------|--------------------|--------------------|--------------------|
| | No calcium sulfate | 1.36 gm. per liter | 0.68 gm. per liter | 0.34 gm. per liter | 0.17 gm. per liter |
| | <i>p. p. m.</i> | <i>p. p. m.</i> | <i>p. p. m.</i> | <i>p. p. m.</i> | <i>p. p. m.</i> |
| A | 5.1 | 8.9 | 8.9 | 8.4 | 7.0 |
| B | 5.2 | 8.9 | 8.8 | 8.1 | 6.8 |

A and B are duplicate experiments.

In order to determine how much calcium sulfate must be present in solution in order to have any appreciable liberation of potash from Dunkirk silt loam, solutions of different concentrations were used and the amount of potash dissolved measured as before. The results are given in table 5.

Figure 1 shows graphically the amount of potash set free at any concentration of solution. It should be noted that 1.36 gm. of calcium sulfate is a third more than will dissolve in a liter of water. This partially explains why half as much of the salt set free as much potash.

The fact that 0.170 gm. of calcium sulfate in a liter of solution, or, in other words, 170 parts per million, made 1.75 parts per million of potash soluble is surprising. If 150 pounds of calcium sulfate were applied to an acre of soil and if the gypsum all dissolved in the moisture in the first foot, at a 20 per cent moisture content the concentration of the calcium sulfate would be approximately 170 parts per million. This may account for the fact that, on

some soils, merely small applications of calcium sulfate have a remarkable action in increasing the crop yields. When large amounts of gypsum are applied to soils the deleterious physical effect of the addition seems to overcome the benefits derived from its use.

Through the kindness of Dr. F. W. Morse, acting-director of the Massachusetts Agricultural Experiment Station, samples of soil were obtained from the plaster and check experimental plots of that station. The soil is of the Merrimac fine sandy loam type, and is considered a very fertile soil. Soil from plot 11 and plot 12, which is the check plot, was obtained. Plot 11 has



FIG. 1. CURVE SHOWING EFFECT OF CONCENTRATION OF CALCIUM SULFATE SOLUTION ON THE SOLUBILITY OF SOIL POTASH

been dressed annually with 800 pounds of "plaster" since 1890. These soils were tested with calcium sulfate solution in the same manner as the other soils, except that the soils remained in contact with the solutions for 5 days only. However, they were shaken more frequently. The results of these experiments are shown below.

As in the following experiments, the calcium sulfate solution used was a saturated solution.

No very definite facts can be deduced from the results of the above experiment, but it seems as if the potash in a soil which has been treated with gyp-

| SOIL | POTASH DISSOLVING IN WATER | | POTASH DISSOLVING IN GYPSUM SOLUTION | |
|--------------------------|----------------------------|-----------------|--------------------------------------|-----------------|
| | A | B | A | B |
| | <i>p. p. m.</i> | <i>p. p. m.</i> | <i>p. p. m.</i> | <i>p. p. m.</i> |
| Plot 11 (plastered)..... | 1.2 | 1.3 | 1.5 | 1.4 |
| Plot 12 (check)..... | 1.0 | 1.0 | 1.2 | 1.5 |

A and B are duplicate experiments.

sum for a large number of years was slightly more soluble than in the untreated soil. This statement requires more conclusive evidence than the above, however, before it can be considered as a fact.

EXPERIMENTS CONCERNING THE SOLUBILITY OF THE SOIL POTASH IN SOLUTIONS OF CALCIUM CARBONATE

Inasmuch as calcium oxide and calcium carbonate are annually added as amendments to the soils of the United States in large quantities, it is important that we know whether or not calcium-carbonate solutions have any similar action on the soil potash. Calcium-carbonate solutions alone were tried (calcium carbonate mixed with soil and distilled water) but because of the very slight solubility of the carbonate the results were negative. They are listed below:

| SOIL | POTASH DISSOLVING IN WATER | POTASH DISSOLVING IN CALCIUM CARBONATE SOLUTION |
|-----------------------------|----------------------------|---|
| | <i>p. p. m.</i> | <i>p. p. m.</i> |
| Whiteland clay subsoil..... | 3.2 | 2.4 |
| Yamhill silt loam..... | 3.0 | 3.0 |

In each case, 2 gm. of calcium carbonate were added to a liter of water. In the case of the Whiteland clay subsoil, the presence of the calcium carbonate seemed to depress the amount of potash going into solution. The results of the analyses checked closely, but it is possible that they are in error. At any rate, there could be no increased solubility of the potash.

Inasmuch as the amount of calcium carbonate going into solution in a soil water is controlled almost entirely by the carbon dioxide which the water contains dissolved in it, it seemed logical to try the solvent action of calcium bicarbonate on soil, or in other words, a solution of calcium carbonate in carbon dioxide and water. In these experiments 125 gm. of Dunkirk silt loam were taken. Two grams of calcium carbonate and a liter of water were added to this soil. The whole was shaken up and kept saturated with carbon dioxide for 5 days, after which the bottles were stoppered up and allowed to stand, with the exception of shaking up once a day for 3 weeks. At the end of this

time the solutions were analyzed for potash, as were the other solutions. The results of these analyses are given in table 6.

For purposes of comparison the check determinations with water and with water saturated with carbon dioxide are given in the table. In the case of Dunkirk silt loam N/50 calcium bicarbonate caused an average increase in solubility of 1.55 parts of potash per million. In cases where a ton or more of lime is added to the acre there may be an appreciable amount of calcium carbonate dissolved in the soil water. In such cases some potash may be affected by the calcium bicarbonate.

TABLE 6

Results showing amounts of potash liberated from Dunkirk silt loam by calcium carbonate solutions

| | SOLUTION | | |
|--------------|-----------------|-------------------------------------|---------------------|
| | Distilled water | Water saturated with carbon dioxide | Calcium bicarbonate |
| | <i>p. p. m.</i> | <i>p. p. m.</i> | <i>p. p. m.</i> |
| A | 5.3 | 8.4 | 9.6 |
| B | 5.2 | 8.7 | 10.8 |
| Average..... | 5.25 | 8.55 | 10.1 |

A and B are duplicate experiments on the same soil.

EXPERIMENTS ON THE SOLUBILITY OF SOIL POTASH IN SOLUTIONS OF VARIOUS SODIUM SALTS

In studying the action of solutions of sodium salts on soils, sodium nitrate, sodium carbonate and sodium chloride were first tried. Table 7 shows the effect of these solutions on Whiteland clay subsoil and Yamhill silt loam.

In the experiment 1.7 gm. of sodium nitrate, 1.169 gm. of sodium chloride and 1.06 gm. of sodium carbonate were taken. The amounts mentioned were enough to give one-fiftieth of an atomic weight of sodium in grams in a liter of solution. These figures certainly show that the soil potash is much more soluble in solutions of these salts than in water. The reason why sodium nitrate should be less active, in this regard, than sodium chloride or sodium carbonate is not clear.

In order to ascertain whether or not other soils were affected similarly by sodium salt solutions, some other soils were tested out in the same fashion. For purposes of comparison, the above-reported results are included in table 8. The amount of salt added was the same in both cases.

The potash in all soils is dissolved to a greater or lesser extent by common salt solutions. The amount going into solution is much greater in the case of the sodium salt solutions than in the case of the calcium sulfate solution or of calcium carbonate solutions. It is noteworthy, that, of the soils listed in

TABLE 7

Results showing the effect of various sodium salts on soil potash

| SOIL | POTASH DISSOLVED BY THE SOLUTION | | | |
|-----------------------------|----------------------------------|-----------------|-----------------|------------------|
| | Distilled water | Sodium nitrate | Sodium chloride | Sodium carbonate |
| | <i>p. p. m.</i> | <i>p. p. m.</i> | <i>p. p. m.</i> | <i>p. p. m.</i> |
| Whiteland clay subsoil..... | 3.2 | 4.9 | 13.3 | 14.3 |
| Yamhill silt loam..... | 3.0 | 8.6 | 22.6 | 22.9 |

TABLE 8

Results showing the effect of sodium chloride on the potash in different soils

| SOIL | POTASH DISSOLVED BY THE SOLUTION | |
|-----------------------------|----------------------------------|-------------------------------|
| | Distilled water | Sodium chloride solution N/50 |
| | <i>p. p. m.</i> | <i>p. p. m.</i> |
| Whiteland clay subsoil..... | 3.2 | 13.3 |
| Yamhill silt loam..... | 3.0 | 22.6 |
| Genessee humus loam..... | 5.5 | 13.0 |
| Durham sandy loam..... | 4.8 | 14.8 |
| Porters sandy loam..... | 3.5 | 14.6 |

TABLE 9

Results showing the effect of the concentration of the sodium chloride solution on the solubility of potash in Yamhill silt loam

| CONCENTRATION OF THE SODIUM CHLORIDE SOLUTION | POTASH DISSOLVED |
|---|------------------|
| <i>grams per liter</i> | <i>p. p. m.</i> |
| 0.0000 | 1.8 |
| 0.0730 | 1.9 |
| 0.1460 | 4.1 |
| 0.2923 | 12.5 |
| 0.5840 | 15.2 |
| 1.1690 | 22.6 |

table 8, the Yamhill silt loam is the most fertile, and that it is also most affected by the sodium chloride solution.

In order to determine the effect of the concentration of the salt solution, the amount of potash going into solution was determined in solutions of sodium chloride of various concentrations. In this experiment a different sample of Yamhill silt loam was used. The results are listed in table 9.

Figure 2 shows the results graphically. It will be noted that the increased solubility of the potash does not amount to much until the concentration of the salt solution reaches about 290 parts per million. At lower concentrations the increased solubility of the potash is hardly noticeable. This may

account for its successful use on beets, whereas it is harmful to a number of other crops. Beets and mangolds need a large amount of potash. They seem to require it in the photosynthesis of sugar. According to Shaw (18) beets are not harmed even when the amount of sodium chloride in the first four feet of an acre rises to 10,000 pounds. Hilgard (15) lists the common crops grown on alkali soils, and sugar beets stand third in order of their resistance to sodium chloride, the only crops surpassing it in this respect being

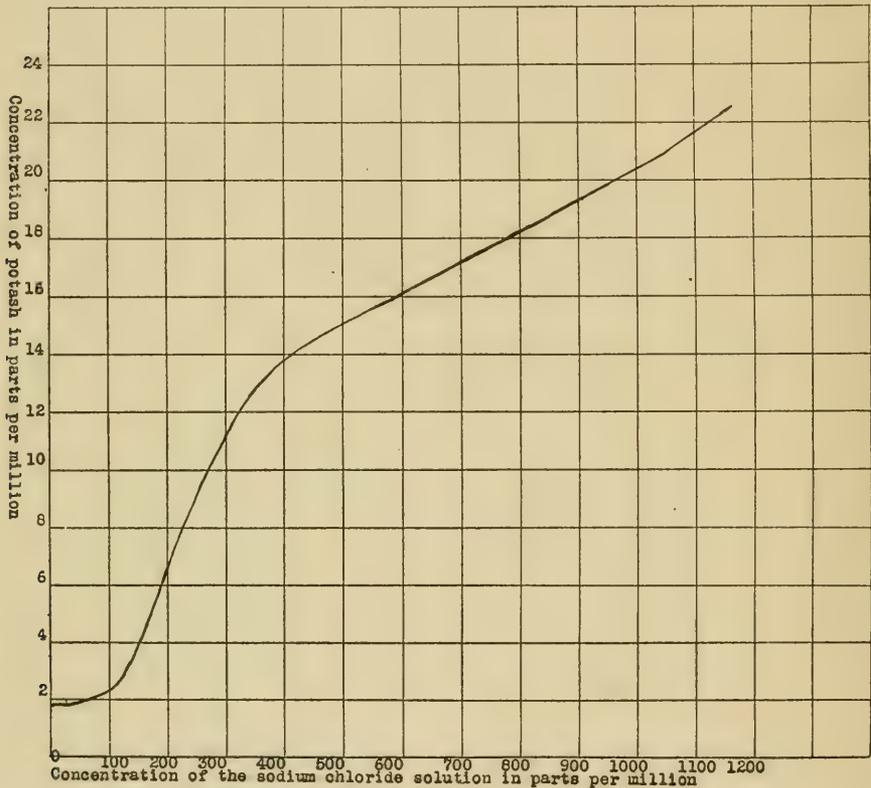


FIG. 2. CURVE SHOWING THE EFFECT OF THE CONCENTRATION OF THE SODIUM CHLORIDE SOLUTION ON THE SOLUBILITY OF SOIL POTASH

salt grass and modiola. Hall (12) advises the use of sodium chloride as a manure for beets, and in England it is a common practice to include sodium chloride in the fertilizers for beets. It may be that the beet, not being harmed by the increased concentration of salt in the soil solution, derives benefit from the potash made soluble by the interaction of the salt with the soil. Such is within the realm of reason, for the concentration of sodium chloride, in the soil solution would only have to rise to about 300 parts per million in order to make considerable potash soluble.

SUMMARY

Certain soils were tried as to their solubility in solutions of the various components of commercial acid phosphate. It was observed that gypsum did exert a solvent action on the potash compounds of the soil. The solubility of the potash in various soils was determined in calcium sulfate solutions. The solubility of the potash in Dunkirk silt loam was determined in solutions of calcium sulfate of various concentrations.

The solubility of the potash in Dunkirk silt loam in solutions of carbon dioxide and calcium bicarbonate was measured.

The action of various sodium salts in making soil potash soluble was observed. The solvent action of sodium chloride solutions on different soils was measured and the effect of the concentration of the sodium chloride solution on the solubility of the soil potash was tested.

CONCLUSIONS

1. If commercial acid phosphate has any action in liberating potash in the soils used in the experiments, it is due to the gypsum which it contains.

2. Calcium sulfate in solution does increase the solubility of the potash compounds in some soils. This action is much more marked on the clay than on the silt or sand. This may explain the fact that only some soils are benefited by applications of gypsum. Calcium sulfate solutions do not seem to be particularly active in dissolving the potash of silt and sands containing mica. It is probable that on some, if not all, fertile clay loam and clay soils, some potash is made soluble by the application of gypsum.

3. In the case of Dunkirk clay loam and silt loam, only a small amount of calcium sulfate need be present in the solution in order to affect materially the solubility of the potash. This may explain why small applications of gypsum are quite beneficial on some soils.

4. The soil potash of Dunkirk silt loam is somewhat more soluble in solutions of carbon dioxide and calcium bicarbonate than it is in a solution of carbonic acid containing the same amount of carbon dioxide. Soils which are high in organic matter may derive some soluble potash from the effect of the calcium bicarbonate in the soil water after the addition of a large amount of lime.

5. Sodium salts are quite active in dissolving potash from soils. The fact that sodium chloride solutions are active in dissolving potash may partially explain why beets derive benefit from applications of salt, since beets are very resistant to the toxic action of sodium chloride. Wheeler points out that beets need sodium for proper growth. These two facts taken together may explain the benefits obtained by the use of salt on certain crops.

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